

PATENT SPECIFICATION

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(54) METHOD FOR THE PREPARATION OF ISO-OLEFIN POLYMERS AND CATALYSTS FOR THE USE THEREIN

(71) We, SUMITOMO CHEMICAL COMPANY LIMITED, a corporation of Japan, of 15, Kitahama 5-chome, Higashi-ku, Osaka, Japan, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a method of polymerising iso-olefins. More particularly, the present invention relates to a method of producing iso-olefin homopolymers or copolymers, e.g. butyl type rubbers, which comprises polymerising or copolymerising an iso-olefin, a mixture thereof, or a mixture of an iso-olefin and polyene in the presence of a particular catalytic system. The present invention also relates to catalysts suitable for use in this process.

A number of catalytic systems for producing butyl type rubbers have hitherto been proposed, for example, metal halide Friedel-Crafts type catalysts have been proposed. Solutions of aluminium chloride in methyl chloride or ethyl chloride have been most frequently used for the production of butyl type rubbers. However, these catalysts required to be used at temperatures as low as about -100°C . Such low temperatures are not desirable from an industrial or economical point of view.

Thus, many attempts have been made to produce, at relatively high temperatures and on a practical scale, iso-olefin polymers having a high degree of polymerisation. For example, it is known to polymerise isobutylene in the presence of a catalyst system of $(\text{C}_2\text{H}_5)_2\text{AlCl}-(\text{tert.}-\text{C}_4\text{H}_9)\text{Cl}$ in a polar solvent such as methylene chloride (Japanese Patent Publication No. 2471/1969) or in the presence of a catalyst system of

$\text{Al}(\text{O sec.}-\text{C}_4\text{H}_9)_3\text{BF}_3-\text{TiCl}_4$
 (J. Polymer Sci., 53, 281).

It is an object of the present invention to

provide iso-olefin homopolymers or copolymers having a high degree of polymerisation and a method for making them.

Another object of the invention is to provide a butyl type rubber having a high molecular weight.

We have found that the use of a catalyst system comprising (1) an aluminium-metal oxide-alkoxide compound and (2) boron trifluoride is effective for producing iso-olefin homopolymers or copolymers having a high molecular weight at higher temperatures than those used when Friedel-Crafts catalysts such as boron trifluoride or aluminium chloride are employed alone.

In accordance with this invention there is provided a method for producing iso-olefin homopolymers or copolymers, which comprises polymerising or copolymerising an iso-olefin, a mixture thereof, or a mixture of iso-olefin and polyene or another polymerisable mono-olefin (except ethylene and propylene) copolymerisable with the iso-olefin in the presence of a catalyst system comprising (1) an aluminium-metal oxide-alkoxide compound represented by the general formula, $\text{M}[\text{OAl}(\text{OR})_2]_2$, wherein M is a divalent metal atom, R is an alkyl radical having from 1 to 8 carbon atoms, an aryl radical having from 6 to 10 carbon atoms, an aralkyl radical having from 7 to 12 carbon atoms, a cycloalkyl radical having from 6 to 10 carbon atoms, or a halogenated derivative thereof, and each R may be the same or different and (2) boron trifluoride.

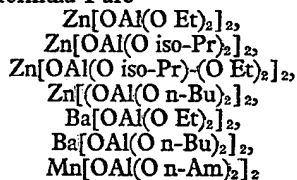
The present invention also provides a catalyst comprising (1) an aluminium-metal oxide-alkoxide compound represented by the general formula, $\text{M}[\text{OAl}(\text{OR})_2]_2$, wherein M is a divalent metal atom, R is an alkyl radical having from 1 to 8 carbon atoms, an aryl radical having from 6 to 10 carbon atoms, an aralkyl radical having from 7 to 12 carbon atoms, a cycloalkyl

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radical having from 6 to 10 carbon atoms, or a halogenated derivative thereof, and each R may be the same or different, and (2) boron trifluoride.

- 5 The divalent metal in the above described formula may be Mg, Ba, Ca, Cd, Cr(II), Mn(II), Fe(II), Co(II) or Ni(II) and R may be methyl, ethyl, propyl, iso-propyl, n-butyl, iso-butyl, sec-butyl, n-amyl, tert-amyl, n-hexyl, n-heptyl, 2-ethylhexyl, 2-chloroethyl, cyclopentyl, cyclohexyl, phenyl, methylphenyl, cresyl or 2-chlorophenyl.

- 10 Representative examples of the aluminium-metal oxide-alkoxide compounds having the general formula I are

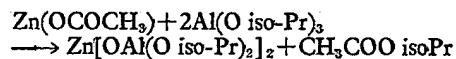


and



- 25 These compounds, when used alone, have no catalytic activity for polymerisation of isobutylene, but when used in combination with boron trifluoride, exhibit a catalytic activity quite different from the known Friedel-Crafts type catalyst, and are effective in the production of polymers of a high degree of polymerisation even at a comparatively high temperature.

- 30 The aluminium-containing compounds are known as catalysts and have been used by I.F.P. (Institut Francais de Petrole) for the production of propylene oxide polymers, and are described by M. Osagan, Ph. Heyssie and J. P. Wauquier in the collection of preliminary reports of Am. Chem. Soc. at Atlantic City Meeting (Sept. 8-13, 1968). The method of synthesizing these compounds is also described in this report. These compounds can be easily synthesized by the reaction of the acetate of a divalent metal with aluminium alkoxide. This reaction can be represented, for example, by the following reaction scheme:



- 50 These compounds are easily soluble in inert organic solvents such as saturated hydrocarbons (for example, n-hexane and n-heptane, and halogenated hydrocarbons (for example, methyl chloride and ethyl chloride), and therefore are convenient for adding to polymerisation systems. During the polymerisation, the further addition of boron trifluoride to the polymerisation system does not cause precipitation of the Al-catalyst, the rate of polymerisation is steady and the catalysts may be advantageously separated after the polymerisation.

The iso-olefins to be used in the present invention may have up to 8 carbon atoms.

Representative examples of these compounds include isobutylene, 2-methyl-1-butene, 3-methyl-1-butene, 2-methyl-2-butene, 4-methyl-1-pentene and mixtures thereof.

The polyenes which are copolymerisable with the above described iso-olefins and which may be used in the present invention include those having from 4 to 14 carbon atoms. Representative examples of these compounds include isoprene, 1,3-butadiene, 2,3-dimethyl-1,3-butadiene, 6,6-dimethylfulvene, piperylene, cyclopentadiene, dicyclopentadiene, divinylbenzene, cyclohexadiene and vinylcyclohexene.

According to the present invention, butyl type rubbery polymers can be obtained by copolymerising a major amount of an iso-olefin, for example in an amount of from 70 to 99.5% by weight, preferably from 85 to 99.5% by weight with a minor amount of a polyene, for example in an amount of from 30 to 0.5% by weight, preferably from 15 to 0.5% by weight. Particularly preferred polymers are obtained by copolymerising from 95 to 99.5% by weight of isobutylene with from 5 to 0.5% by weight of isoprene.

Iso-olefins can be homopolymerised to produce useful polymers. For example, isobutylene, when polymerised alone, forms polyisobutylene having a high degree of polymerisation. Iso-olefins may be also copolymerised with other polymerisable mono-olefins such as styrene.

Further, by the use of the catalyst system of the present invention, useful, low molecular weight polymer can also be obtained if desired. Thus, when a considerable amount of polyene for example 30 to 5% by weight of isoprene, is copolymerised with an iso-olefin, for example 70 to 95% by weight of isobutylene, at any desired temperature, butyl rubbers having a low, number average molecular weight of 1,000 to 50,000 may be produced in syrup- or grease-like form. As they have a narrow molecular weight distribution, they are low in spinnability and are therefore easy for processing into elastic sealants with or without dilution in a solvent. After the vulcanisation they have a high strength. This seems to be due to the comparatively uniform length of the molecules.

The polymerisation is generally conducted in an inert solvent so as to facilitate the operation. Any type of solvent which is inert under the polymerisation conditions can be used. Examples of such solvents are conventional halogenated hydrocarbons (for example, methyl chloride, ethyl chloride, chlorobenzene, methyl bromide and carbon tetrachloride), carbon disulphide, saturated hydrocarbons (for example, n-hexane and n-heptane), unsaturated hydrocarbons (for example, ethylene and propylene), aromatic hydrocarbons (for example, benzene and toluene) and mixtures thereof. The amount of the catalyst to be used in the present invention may range from 2 to 0.001% by mole, preferably from 1 to 0.01% by mole for the

aluminium-metal oxide-alkoxide compound and from 10 to 0.001% by mole, preferably from 5 to 0.02% by mole, for boron trifluoride, based on the starting material.

5 For carrying out smoothly the method of the present invention, either bulk or solution polymerisation can be selected, and the polymerisation may be conducted batchwise or continuously.

10 When carrying out a polymerisation by using the catalyst system of the present invention, the polymerisation can be accelerated or controlled by the presence of a polar substance such as water, alcohols and organic carboxylic acids.

15 Such has been well known for the Friedel-Crafts type catalysts and this is also the case for the catalytic system of this invention.

20 The polymerisation temperature to be used in the polymerisation system of the present invention is generally below 0°C. A dominant characteristic of the present invention consists in that the catalyst system of the invention provides high molecular weight polymers at a higher temperature than that used in the case of the conventional Friedel-Crafts type catalysts, but by lowering the polymerisation tem-

perature it is possible to increase the degree of polymerisation further. Thus, the temperature can be suitably selected over a wide range according to the desired molecular weight of the polymer.

To illustrate the method of the present invention, the following examples are given.

Examples 1—5 and

Comparative Example 1.

To a 300 ml. flask, 33.7 g. isobutylene and 150 ml. n-heptane were charged. Further, 0.5 millimole of aluminium-metal oxide-alkoxide of the general formula $M[OAl(OR)_2]_2$ was added. Then, an amount of boron trifluoride as shown in Table 1 was introduced into the upper space of the flask while being stirred and cooled. After polymerisation for one hour, ethanol was added to stop the reaction. On freeze-drying the thus-obtained polymerisate for one day, a white rubbery polymer was obtained. The results are shown in Table 1 together with the result obtained in Comparative Example 1 in which aluminium-metal oxide-alkoxide was not added.

TABLE 1

Example	1	2	3	4	5	Comp. Example 1
Aluminium-metal oxide-alkoxide* (0.5 millimole)	A	B	C	D	E	
BF ₃ (millimole)	5.3	6.8	5.5	6.2	6.5	4.0
Polymerisation temperature (°C)	-65	-65	-65	-65	-65	-65
Yield (g.)	29.5	26.5	31.0	25.0	23.2	23.1
Viscosity average molecular weight (thousand)	1210	950	1100	800	750	95

* A = $Zn[OAl(O \text{ iso-Pr})_2]_2$

B = $Zn[OAl(O \text{ iso-Pr})(O \text{ Et})]_2$

C = $Mn[OAl(O \text{ n-Am})_2]_2$

D = $Ba[OAl(O \text{ n-Bu})_2]_2$

E = $Cd[OAl(O \text{ Et})_2]_2$

Examples 6—8 and
Comparative Example 2.

5 To a 300 ml. flask, 33.7 g. isobutylene, 0.68 g. isoprene and 150 ml. n-heptane were charged. Further, 0.5 millimole of aluminium-metal oxide-alkoxide of the general formula $M[OAl(OR)_2]_2$ was added and then cooled to a temperature of -65°C . Whilst this reaction liquid was stirred, BF_3 was introduced

into the upper space of the flask. After polymerisation for one hour, ethanol was added to stop the reaction. On freeze-drying the thus obtained polymerisate for one day, a rubbery polymer was obtained. These results are shown in Table 2 together with the result in Comparative Example 2 in which aluminium-metal oxide-alkoxide was not added. 10 15

TABLE 2

Example	6	7	8	Comp. Example 2
Aluminium-metal oxide-alkoxide* (0.5 millimole)	A	B	C	
BF_3 (millimole)	3.5	4.5	3.0	4.0
Polymerisation temperature ($^\circ\text{C}$.)	-65	-65	-65	-65
Yield (g.)	31.5	31.2	27.8	23.5
Viscosity average molecular weight (thousand)	530	320	430	12
Double bond content (isoprene mole %)	1.10	1.03	1.23	1.20

* A = $\text{Zn}[OAl(O\text{-}n\text{-Bu})_2]_2$

B = $\text{Ba}[OAl(O\text{-}Et)_2]_2$

C = $\text{Zn}[OAl(O\text{-}iso\text{-}Pr)_2]_2$

Examples 9—10 and
Comparative Example 3.

20 To a 300 ml. flask, 33.7 g. isobutylene, 0.68 g. isoprene and 150 ml. methyl chloride were charged. Further, 0.5 millimole of aluminium-metal oxide-alkoxide was added, and an amount of BF_3 as shown in Table 3 was introduced into the upper space of the flask while 25

being stirred and cooled. After polymerisation for one hour, ethanol was added to stop the reaction. On freeze-drying the thus obtained polymerisate, white rubbery polymer was obtained. These results are shown in Table 3 together with the result of Comparative Example 3 in which aluminium-metal oxide-alkoxide was not added. 30

TABLE 3

Example	9	10	Comp. Ex. 3
Aluminium-metal oxide-alkoxide (0.5 millimole)	$\text{Zn}[\text{OAl}(\text{O iso-Pr})_2]_2$	$\text{Zn}[\text{OAl}(\text{O Et})_2]_2$	
BF_3 (millimole)	3.2	4.3	4.0
Polymerisation temperature (°C.)	-75	-75	-75
Yield (g.)	28.1	30.1	30.2
Viscosity average molecular weight (thousand)	720	650	98
Double bond content (isoprene mole %)	1.15	1.21	1.23

5 It is apparent from Examples 1 to 10 that according to the method of the present invention polymers of higher molecular weight than those obtained in Comparative Examples 1 to 3 in which BF_3 catalyst was used alone can be obtained.

Examples 11 and 12.

10 To a 300 ml. flask, predetermined amounts of 2-methyl-1-butene or 2-methyl-1-butene and isoprene as shown in Table 4 were charged,

and 150 ml. methyl chloride was added. Then, 0.5 millimole of $\text{Zn}[\text{OAl}(\text{O iso-Pr})_2]_2$ was added and a predetermined amount of BF_3 as shown in Table 4 was introduced into the upper space of the flask while being stirred and cooled. After polymerisation for one hour, isopropyl alcohol was added to stop the reaction. The thus-obtained polymer was dissolved in benzene, and on freeze-drying for one day a white polymer was obtained. The results are shown in Table 4.

15

20

TABLE 4

Example	11	12
BF_3 (millimole)	4.1	4.5
2-Methylbutene-1 (g.)	30.1	30.1
Isoprene (g.)	—	6.0
Polymerisation temperature (°C.)	-45	-45
Viscosity average molecular weight (thousand)	210	100
Double bond content (isoprene mole %)	—	0.6

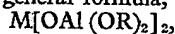
Example 13.

To a 300 ml. flask, 33.7 g. isobutylene and 2.55 g. isoprene were charged, to which 150 ml. n-heptane and then 0.5 millimole
 5 $\text{Zn}[\text{OAl}(\text{O iso-Pr})_2]_2$ were added. After cooling the mixture to -75°C . while being stirred 9 millimoles of BF_3 were added. After polymerisation for two hours methanol was added to stop the reaction. On drying under reduced
 10 pressure at 55°C ., 31.5 g. of a semi-fluid polymer were obtained. The double bond content was 4.2 isoprene mole percent, the viscosity average molecular weight 28,000 and the molecular weight distribution coefficient
 15 (weight average molecular weight/number average molecular weight) 3.5.

When polymerisation in this example was carried out without $\text{Zn}[\text{OAl}(\text{O iso-Pr})_2]_2$ and with only BF_3 , the yield of the polymer was 29.5 g., the viscosity average molecular weight 8,000 and the molecular weight distribution coefficient 10.3.

WHAT WE CLAIM IS:—

1. A method for producing iso-olefin homo-
 25 polymers or copolymers, which comprises polymerising or copolymerising an iso-olefin, a mixture thereof, or a mixture of iso-olefin and polyene or another polymerisable mono-
 30 olefin (except ethylene and propylene) copolymerisable with the isoolefin in the presence of a catalyst system comprising (1) an aluminium-metal oxide-alkoxide compound represented by the general formula,



35 wherein M is a divalent metal atom, R is an alkyl radical having from 1 to 8 carbon atoms, an aryl radical having from 6 to 10 carbon atoms, an aralkyl radical having from 7 to 12 carbon atoms, a cycloalkyl radical
 40 having from 6 to 10 carbon atoms, or a halogenated derivative thereof, and each R may be the same or different, and (2) boron trifluoride.

2. A method according to Claim 1 wherein the iso-olefin is isobutylene, 2-methyl-1-butene,
 45 3-methyl-1-butene, 2-methyl-2-butene, 4-methyl-1-pentene or any mixture thereof.

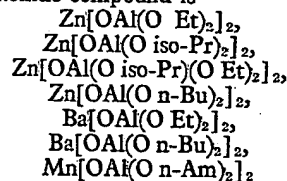
3. A method according to Claim 1 or Claim 2 wherein the polyene is isoprene, 1,3-butadiene, 2,3-dimethyl-1,3-butadiene, 6,6-dimethylfulvene, piperylene, cyclopentadiene, di-
 50 cyclopentadiene, divinylbenzene, cyclohexadiene or vinylcyclohexene, or the mono-olefin is styrene.

4. A method according to any one of the preceding claims wherein iso-olefin copolymers
 55 are obtained by copolymerising from 70 to 99.5% by weight of an iso-olefin with from 30 to 0.5% by weight of a polyene.

5. A method according to Claim 4 where-

in iso-olefin copolymers are obtained by co-
 60 polymerising from 95 to 99.5% by weight of isobutylene with from 5 to 0.5% by weight of isoprene.

6. A method according to any one of the preceding claims wherein the aluminium-metal
 65 oxide-alkoxide compound is



or



7. A method according to any one of Claims 1 to 5 wherein the divalent metal atom is Mg, Ba, Ca, Cd, Cr(II), Mn(II), Fe(II), Co(II) or Ni(II).

8. A method according to any one of the preceding claims wherein the aluminium-metal
 80 oxide-alkoxide compound is used in an amount of from 2 to 0.001% by mole based on the starting monomer.

9. A method according to any one of the preceding claims wherein boron trifluoride is
 85 used in an amount of from 10 to 0.001% by mole based on the starting monomer.

10. A method according to any one of the preceding claims wherein the polymerisation
 90 or copolymerisation is carried out in the presence of a solvent.

11. A method according to Claim 10 wherein the solvent is methyl chloride, ethyl chloride, chlorobenzene, methyl bromide, carbon tetra-
 95 chloride, carbon disulphide, n-hexane, n-heptane, ethylene, propylene, benzene or toluene.

12. A method according to any one of the preceding claims wherein the polymerisation
 100 or copolymerisation is carried out at a temperature below 0°C .

13. A method of producing iso-olefin homopolymers or copolymers according to Claim 1
 105 and substantially as hereinbefore described in any of the Examples.

14. An iso-olefin homopolymer or copolymer whenever produced by the method of any one
 of the preceding claims.

15. A catalyst comprising (1) an aluminium-metal oxide-alkoxide compound represented
 110 by the general formula, $\text{M}[\text{OAl}(\text{OR})_2]_2$, wherein M is a divalent metal atom, R is an alkyl radical having from 1 to 8 carbon atoms, an aryl radical having from 6 to 10 carbon atoms, an aralkyl radical having from 7 to 12 carbon atoms, a cycloalkyl radical having from 6 to 10 carbon atoms, or a halogenated substitute thereof, and each R may be the same or different, and (2) boron trifluoride.

STEVENS, HEWLETT & PERKINS, ..
Chartered Patent Agents,
5, Quality Court,
Chancery Lane, London, W.C.2,
Agents for the Applicants.

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